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METHOD FOR SELECTIVE HYDROGENATION OF NAPHTHALENE

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Claim

A method for selective hydrogenation of naphthalene, characterized in that in hydrogenation of alkylnaphthalene or naphthalene to alkyltetralin or tetralin, the catalyst for hydrogenation-desulfurization is used by fixed bed mode, furthermore, an organic compound, which thoroughly dissolves alkylnaphthalene or naphthalene and easily vaporizes under the hydrogenation reaction condition, is used as a diluent for raw materials.

Detailed explanation of invention

The present invention relates to a method for converting alkylnaphthalene or naphthalene to alkyltetralin or tetralin by selective hydrogenation.

Tetralin obtained by partial hydrogenation of naphthalene is fit for various uses such as solvents of various types of paints and varnishes, degreasing of fibers, removal of printing ink, and others due to a high boiling point and high dissolving power and its potential demand is large, but an economically satisfactory industrial production method for tetralin has not been known up to now.

In the hydrogenation of naphthalene to tetralin, the generation of heat is as high as 250 kcal/kg, and as the reaction temperature goes up, the selectivity of tetralin decreases and the production amount of decalin secondary product suddenly increases at 300°C or higher, as is clear even from the literature (C. G. Frye, A. W. Weitkamp, Journal of Chemical and Engineering Data, vol. 14, No. 3, p. 372, 1969 and Shingyu Ando, Kinori Ushiba, Takefumi Kuroda, Masao Saeki, Coal Tar, vol. 15, No. 9, p. 25, 1963).

Namely, to make the reaction rate or conversion to tetralin high and also make the tetralin selectivity satisfactory, a method of controlling the reaction temperature at a suitable temperature by avoiding a sudden temperature increase by the reaction heat is needed. Typical ones for the above method are a method of removing the reaction heat as sensible heat of catalyst slurry by the fluidized catalyst process disclosed in US Patent No. 2,481,921 and a method of dividing the conversion rate into a small fraction by serially arranging many adiabatic fixed-bed reactors and repeating the reaction and cooling to control the reaction temperature width to a narrow range disclosed in US Patent No. 3,541,169. The above are superior in the operation to the conventional batch type liquid phase reaction method since the reaction is carried out in the gas phase, but the device becomes complicated and the facility cost increases.

Further, in the conventional method for production of tetralin, it was necessary to remove the sulfur impurity in raw naphthalene since catalysts liable to be poisoned by sulfur, for example, nickel or platinum type catalysts, were used. Said catalysts are preferred from the standpoint of tetralin selectivity since they are active at low temperatures of about 200°C, but they are not economical because of the difficulty in use with tar type naphthalene and the necessity of desulfurization prior to hydrogenation in the case of using low-sulfur petroleum type naphthalene.

For example, in the aforementioned US Patent No. 2,481,921, a method of continuously removing the catalyst consumed in nickel sulfide form and replenishing new catalyst is employed. Further, in US Patent No. 3,541,169, a method of desulfurizing with copper oxide catalyst is employed. However, the operation becomes complicated even if only by the regeneration of catalysts in both cases.

The present invention overcomes the aforementioned two disadvantages and provides a method of extremely economically obtaining alkyltetralin or tetralin from alkyl naphthalene or naphthalene. Namely, the present invention provides a method of obtaining alkyltetralin or tetralin by diluting alkyl naphthalene or naphthalene in a solvent and passing it as a gas-liquid mixed phase through a fixed-bed reactor packed with a catalyst for hydrogenation-desulfurization.

Here, the solvent, which is the first special feature of the present invention, refers to organic compounds, which have high solubility of alkyl naphthalene and naphthalene, and exist mostly in a liquid state at the lowest reaction temperature but mostly in a gas state at the highest reaction temperature, namely, are easily vaporized at the hydrogenation condition. The application purpose of the solvent is to reduce the temperature increase caused from the reaction heat by utilization of vaporization latent heat of the solvent. If the reaction conditions are in the range of 250-330°C and 30-60 kg/cm², aromatic hydrocarbons with carbon number of 6-9, such as benzene, toluene, xylene, ethylbenzene, ethyltoluene, and the like and their mixtures are desired from the consideration of critical temperature and critical pressure. Said aromatic hydrocarbons also have an advantage in that they are easily separated and recovered by simple distillation after the reaction to use them again since the boiling point difference between the aromatic hydrocarbons and tetralin is large.

The catalyst for hydrogenation-desulfurization, which is the second special feature of the present invention, refers to catalysts for hydrogenation and desulfurization of various petroleum fractions such as naphtha, kerosene, heavy oil and the like, catalytic cracking oil fractions, and thermal cracking oil fractions. It is well known that various types of catalysts have been developed in recent years due to the air pollution problem or quality problem of petroleum type fuels. Said are catalysts obtained by carrying oxides of Group VII metals such as iron, cobalt,

nickel, and the like or oxides of Group VI metals such as molybdenum, tungsten, and the like or their mixtures on alumina or silica-alumina, and in many cases they are used by pre-sulfidizing with hydrogen sulfide or organic sulfur compounds.

Raw naphthalene to be used in the present invention method is not limited to only that from catalytically reformed oil or catalytically decomposed oil through a dealkylation process or that separated from naphtha cracking oil or crude oil cracking oil, but tar system naphthalene with high sulfur content also can be used. In the case of those containing impurities having a boiling point close to that of tetralin, for example, 4-methylindan (202°C), 5-methylindan (205°C), 1,2,3,4-tetramethylbenzene (205°C), and the like, it is desired to remove said impurities by a method such as distillation beforehand.

Further, since the solvent for dilution and unreacted naphthalene are recovered by distillation after hydrogenation and reused by recycling in the present invention method, it is not necessary to make the reaction rate close to 100%, rather it is desired to select various conditions such as pressure, temperature, hydrogen flow rate, liquid space velocity, raw naphthalene concentration, type of solvents, and the like for raising the reaction rate as much as possible within the tetralin selectivity range of 95% or higher.

Furthermore, as mentioned earlier, the present invention method is not limited to a method of simply producing tetralin from naphthalene but it can be applied to a method of producing alkyltetralin by selectively hydrogenating general alkyl naphthalene such as methyltetralin from methyl naphthalene, dimethyltetralin from dimethyl naphthalene, and the like, and its special feature and advantage are all common.

Hereinafter, the present invention is explained in detail by typical application examples and comparative examples, but the present invention is not limited to those only.

In the application examples and comparative examples, the following experiment was carried out using an external electric heating type stainless steel reactor with an inner diameter of 35 mm and length of 1500 mm, an air-liquid separator with an inner diameter of 50 mm and length of 1000 mm, and a continuous hydrogenation device comprising a plunger pump, hydrogen pump and relief valve. Furthermore, the reactor was divided into a 230-mL (volume) preheating section packed with glass beads with 3-5 mm diameter and a 1000-mL (volume) catalyst-packed reaction section below the preheating section, and the reaction temperature at each part of the packed catalyst was measured by 5 thermocouples and adjusted by an external heater divided into 5 parts. Raw oil and hydrogen were supplied in a countercurrent manner.

Application examples 1-8

A catalyst (124-1.5E, GC-4-1.5E or 153-3E), Nippon Ketchen Co., 1000 ml for hydrogenation-desulfurization was packed into a reactor, pressurized at room temperature to

hydrogen sulfide partial pressure 1 kg/cm², hydrogen partial pressure 14 kg/cm² and total pressure 15 kg/cm², heated to 250°C, kept at the temperature for 3 h and sulfidized. The characteristics of the catalysts used are shown in Table 1.

Unreacted hydrogen sulfide was expelled and the reactor was sufficiently replaced with hydrogen. Then, tar system naphthalene on the market shown in Table 2 was hydrogenated under the condition shown in Table 3 to convert to tetralin at high conversion and high selectivity. Furthermore, as diluents, the toluene had a purity of 99.9% or higher and the xylene was a mixture of ethylbenzene (43%), p-xylene (14%), m-xylene (31%) and o-xylene (12%), and the sulfur content in both diluents was 0.1 ppm or less.

Then, the hydrogenation solutions in Application Examples 1-3 were mixed and after removing xylene by simple distillation, it was rectified in a Macmahon-packed rectifier with 25 theoretical plates at a reflux ratio of 10 to obtain tetralin as a 205-207°C fraction, the purity of which was 98.9%.

Table 1

Catalyst name		124-1.5E	GC-4-1.5E	153-3E
Physical properties	Diameter, mm	1.5	1.6	2.5
	Average length, mm	4.0	4.0	5.0
	Apparent specific Gravity	0.75	0.70	0.67
Chemical compositions wt %	CoO	4.0	1.5	0
	MoO ₃	12.0	16.5	15.0
	NiO	0	3.0	3.0
	SiO ₂	1.0	1.0	1.1
	Na ₂ O	0.06	0.06	0.07
	Fe	0.06	0.02	0.04
	SO ₄	2.0	2.0	2.0
	Al ₂ O ₃	balance	balance	balance

Table 2

	Refined naphthalene	Crude naphthalene	Analytical method
Maker	Nisshin Kasei Co.	Sumikin Coke & Chemicals	
Composition (%)			
Naphthalene	98.7	96.6	Gas chromatography
Thionaphthalene	1.3	3.4	PEG column
Solidification point (°C)	79.8	78.5	Sumika method
Sulfuric acid coloration	3 (-)	3 (+)	JIS K2421
Water content (%)	0.013	0.023	Karl Fischer method
Non-volatiles (%)	0.01	0.04	JIS K2421
Total sulfur (%)	0.20	0.66	Wickbold method

Table 3

	1	2	3	4	5	6	7	8
Feed solution								
Raw naphthalene*	A	A	B	A	A	B	A	B
Dilution solvent**	X	X	X	X	T	X	T	T
Naphthalene concentration (wt%)	20	25	20	20	20	20	25	25
Solution sulfur content (ppm)	470	490	960	480	470	510	490	1050
Reaction condition								
Catalyst***	a	a	a	b	b	b	c	c
Reaction temperature, highest	300	312	301	305	306	299	314	317
(°C) lowest	293	300	293	295	294	288	299	303
Reaction pressure (kg/cm ²)	49	50	49	49	50	50	48	50
Liquid space velocity (l/l/h)	1.5	2.1	1.5	1.5	1.5	1.5	2.3	2.1
Exit hydrogen flow rate (NI/h)	210	230	210	230	230	210	210	230
Reaction results****								
Naphthalene conversion %	92.5	91.9	92.8	97.7	95.5	90.6	93.1	89.4
Tetralin selectivity %	94.0	97.1	93.6	96.9	97.3	98.4	95.5	98.2
trans-Decalin selectivity %	4.2	2.2	4.4	2.6	2.3	1.2	3.8	1.4
cis-Decalin selectivity %	1.8	0.7	2.0	0.5	0.4	0.4	0.7	0.4
Solution sulfur content (ppm)	40	43	320	27	29	31	22	290

- * raw naphthalene A: refined naphthalene from Nisshin Kasei Co.
 B: crude naphthalene from Sumikin Coke &
 Chemical Co.
- ** dilution solvent X: xylene
 T: toluene
- *** catalyst (Nippon Ketchen Co.) a: 124-1.5E
 b: GC-4-1.5E
 c: 153-3E
- **** The composition analysis was carried out by gas chromatography.
 Apiezon L column, 3 m, column temperature 165°C, carrier gas:
 helium 70 mL/sec.

Comparative Example 1

When a 20 wt% solution prepared by dissolving refined naphthalene in commercial tetralin (Wako Pure Chemical Industries Co., purity 98.2%) was fed under the conditions of the same catalyst, pressure, liquid space velocity, and exit hydrogen throughput as in Application Example 1 and the inlet temperature of the catalyst section was raised to 280°C, the heat generation was large and the temperature at each catalyst section suddenly increased to 350°C or higher, so that it could not be controlled even when the outer part of the reactor was air cooled, and it reached a dangerous state.

Comparative Example 2

When the same 20 wt% solution as that in Comparative Example 1 was fed under the conditions of the same catalyst, pressure, liquid space velocity, and exit hydrogen throughput as in Application Example 5 and the inlet temperature of the catalyst section was raised to 270°C, the heat generation was large so that the reaction temperature could not be controlled and the catalyst partially collapsed, and thus black solids were precipitated in the solution removed from the reactor.

Application Example 9

A 20 wt% solution, prepared by dissolving naphthalene (purity 98.2 wt%, total sulfur content 4 ppm) separated as a by-product from heavy oil in a naphtha decomposing ethylene plant in xylene, was fed under the conditions of the same catalyst, pressure, liquid space velocity, and exit hydrogen throughput as in Application Example 1 and hydrogenated at a temperature of 290-296°C to obtain a naphthalene conversion of 96.1% and tetralin selectivity of 93.5%.